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Ion exchanged Fe-FER through H_2O_2-assisted decomplexation of organic salts†

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Decomplexation of organic ligands through redox titration has been applied to catalyst synthesis, developing an improved preparation method for Fe-ferrierite (Fe-FER), the catalyst showing excellent performance and durability for N_2O decomposition under realistic conditions for nitric acid plants.

N_2O is nowadays mainly emitted by the nitric acid industry as an unwanted by-product. Direct *end-of-pipe* decomposition of the tail gas is a cost-effective technology.[1] The estimated costs of this reduction technology is much lower than most CO_2 reduction technologies. For the Netherlands the abatement of the nitric acid plant N_2O emissions can already meet 30% of the Kyoto targets. Legislation will come soon and the market of N_2O-decomposition catalysts is developing. Since the pioneering work of Feng and Hall[2] on over-exchanged FeZSM-5 catalysts, Fe-MFI catalysts have been widely studied and optimised for N_2O decomposition and selective catalytic reduction of NO. Different preparation methods have been developed, including wet ion exchange (WIE),[2] sublimation of $FeCl_3$ (CVD),[3,4] solid-state ion exchange (SSIE),[5] and isomorphous substitution of Fe into the MFI framework and extraction by steaming.[6] The discussion in the literature has been mainly focused on the reproducibility of the preparation method and the structure of the iron sites. The study on new zeolite matrices has received much less attention. Iron exchanged ferrierite (Fe-FER) has been claimed to be very active for N_2O decomposition by ion exchange.[7] WIE appears to be the easiest preparation method to apply commercially. It can be controlled by accessible experimental parameters, resulting in very reproducible preparations.

According to WO 99/34901[7] catalysts are prepared *via* ion-exchange using ferric nitrate and NH_4–ferrierite, yielding the most active state-of-the-art Fe-catalyst for N_2O decomposition known. However, one important issue that remains unresolved is the waste generated during manufacturing (nitrates and NOx). Nitrates in waste water lead to eutrophication (massive growing of algae) in the emitted water. Denitrification is expensive since facultative heterotrophic bacteria are conventionally used for that. Sulphates are also employed. They also present similar problems as nitrates.

Alternatively, the use of organic Fe precursors which yield CO_2 (instead of NO_x) and water during calcination will minimise the waste generated. Preliminary studies using iron citrate, acetate and oxalate revealed that the performance of these catalysts was inferior to the conventionally exchanged ferric nitrate ones. Organic salts form stable complexes with Fe cations, which hinder the exchange process. Such problem has already been reported and studied by Marturano *et al.*[8] on Fe(II)-oxalate over ZSM-5. Uncharged species $[Fe(C_2O_4)(H_2O)_4]$ accounted for *ca.* 30% of the total iron in solution. Additionally, the remaining $[Fe(H_2O)_6]^{2+}$ was not able to be fully exchanged on the zeolite since the oxalate complex was also blocking the zeolite pore mouths.

The concept presented here is to break down complexation equilibria by titrating the chelates with H_2O_2. The removal of ligands liberates Fe^{3+} cations and/or partially charged Fe(III) hydroxocomplexes. The exchange is expected to be improve.

A set of catalysts was prepared using iron citrate ($FeC_6H_5O_7$, SIGMA) as a precursor with 0.5 *wt* % iron loading. The choice of this salt was based on the solubility in water and cost. The complexation of citrates to Fe(III) is very strong, log $K_{ML/M\cdot L}$ = 11.5, against 3.05 for Fe(II)-oxalate,[9] which makes the citrate removal most challenging as being one of the worst cases. Additionally, citrate groups are bigger than oxalate ones (Fig. 1), which make its use for ion-exchange more difficult as they can block the entrance of the zeolite channels.

The Fe solution containing the desired amount of Fe (0.5 wt.% in the final catalyst) was prepared and added to the zeolite (NH_4-FER, TOSOH Si/Al = 9), forming a kind of slurry containing the Fe precursor. Then, the appropriate amount of diluted H_2O_2 (Merck) was added to the slurry (molar ratio H_2O_2/citrate = 40). The total volume of the liquid added corresponded with *ca.* 150% of the pore volume of the zeolite. This approach is already known for impregnation (incipient wetness) but it is not normally applied in ion-exchange, where usually a large excess is used. The reaction time could be reduced to *ca.* 1 h including drying of the sample. Typically, ion-exchange is carried out for a much longer time (12–24 h). The N_2O-decomposition performance did not improve for longer times (not shown). After titration, the sample was dried at 373 K in the synthesis vessel for 2 h, and no washing was carried out. The sample was calcined at 823 K for 6 h.

The catalyst's performance was tested in the decomposition of N_2O. Temperature is very important during the titration reaction

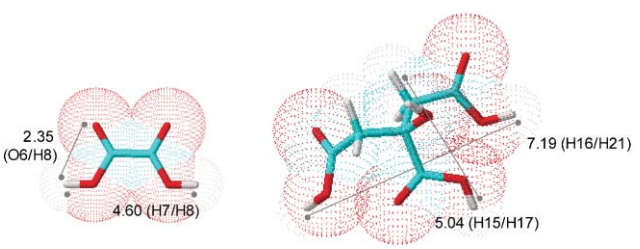

Fig. 1 3-D structures of oxalic (left) and citric acid molecules. Distances are in angstroms.

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with hydrogen peroxide. Fine-tuning experiments were performed at different temperatures: 333, 353 and 373 K. Fig. 2 shows the N_2O conversion level at 673 K for different titration temperatures. The optimal temperature was around 353 K. The activity level was even higher than the reference catalyst (Fe-FER prepared by conventional ion exchange, according to WO 99/34901[7]). An intermediate temperature (*ca.* 353 K) is optimal to break down the complexation equilibria efficiently, and in a controlled fashion. The obtained results are not straightforward. Many phenomena occur during the removal of the ligands, for instance the hydrolysis of metal cations.[10] Once the ligands are being removed, the metal cation starts to hydrolyse (Fe(III) to $FeO(OH)_x$), which in the end gives inactive hydroxide species. The complexity of the situation may refrain people from using oxidising agents to remove ligands in catalyst preparation. Currently, research is ongoing to further clarify the effect of the synthesis parameters. It can be assumed that at lower temperatures the titration is slow and therefore not all the citrate complexes have decomposed. At the highest temperature, the kinetics of the titration is that fast that the Fe-exchange with the zeolite is too slow and the excess Fe^{3+} is hydrolysed to $Fe(OH)_3$, which yields inactive species for N_2O decomposition. So, an intermediate temperature, where a balance between these competing processes is obtained, allows an optimal synthesis. Fenton-like oxidation involving hydroxyl radicals can occur as well. Ferric salts in the presence of H_2O_2 generate $OH^{\bullet}$ radicals which are strongly oxidizing agents. The rate of oxidation depends on the initial concentration of ferric ions. According to thermodynamic predictions of ferric citrate solutions, the presence of free Fe^{3+} is not negligible at the synthesis conditions employed. Therefore, both direct H_2O_2 and hydroxyl radicals may be involved during titration.

The Fe species in the catalyst have been characterised by TPR in the optimal catalyst (Figure 3). The Fe species detected are similar to those typically encountered in the ion-exchanged catalysts using Fe-nitrates: Fe–hydr(oxo) complexes stabilised in the zeolite cavities.[11,12] Although the relative intensities of the peaks are

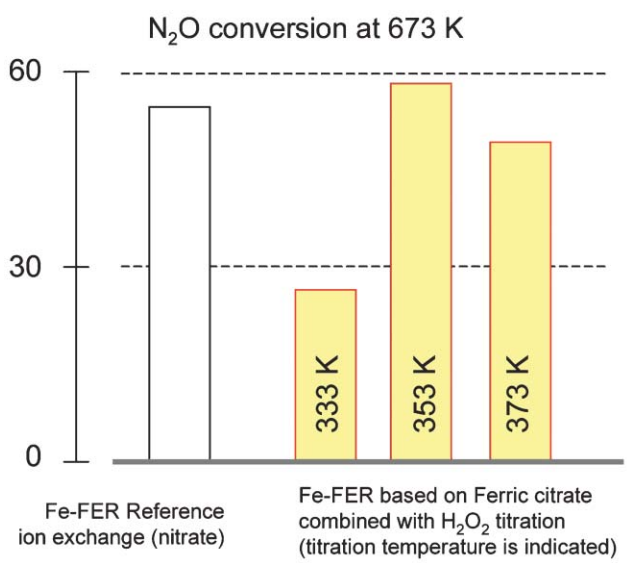

Fig. 2 Effect of the titration temperature during the preparation of the Fe-citrate FER catalysts. The performance (N_2O/He) is compared with the reference catalyst prepared by WIE (Fe-FER ion exchange, ferric nitrate).

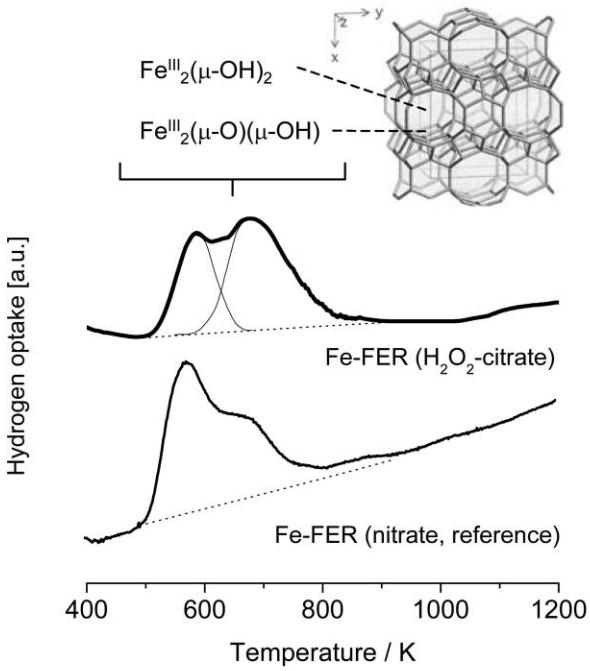

Fig. 3 Temperature-programmed reduction profiles of both Fe-citrate (353 K) and Fe-nitrate FER catalysts. Location of the peaks proves that the Fe-species involved are exchanged Fe-complexes.

different, it is clear that exchanged species are formed. No traces of (inactive) FeO_x clusters, that reduce at higher temperatures, were detected. The structure of the active Fe-complexes for this reaction is still under lively debate. The current work does not shed new light on this aspect.

The stability of the optimized catalyst (Fe-FER, H_2O_2-citrate-353) was tested under simulated conditions of a nitric acid plant for 45 h on-stream, including the presence of NO, O_2 and H_2O together with N_2O. The results obtained were excellent. It shows high stability (no deactivation, activity loss <2%) under such conditions.

The innovative aspect of the presented study is the use of a mild oxidant (H_2O_2) to remove organic ligands present in solution during catalyst preparation. Strong complexating equilibria can be overcome during ion-exchange by controlled redox titration of the ligands. Hydrogen peroxide oxidizes citrate groups effectively, releasing Fe species at a controlled rate. This opens new ways to use organic salts of the metals in catalyst synthesis, which only renders water and carbon dioxide during titration. Additionally, hydrogen peroxide is decomposed in water and oxygen, which makes the preparation environmentally very attractive. As catalysts are specialty products, the market price of H_2O_2 is less critical than is usually the case in the chemical industry.

In conclusion, we have developed a new synthesis route involving less waste water, much shorter synthesis time and less undesired gas emissions in calcination. The H_2O_2–citrate Fe-FER is a greener synthesis route and an example of *process intensification*.[13] An *intensified process* involves for instance less energy consumption, shorter time-to-market, but it does also require less waste emissions. Both aspects of the current study, the preparation

and application of the catalyst in N_2O abatement, contribute to an *intensified* technology.

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